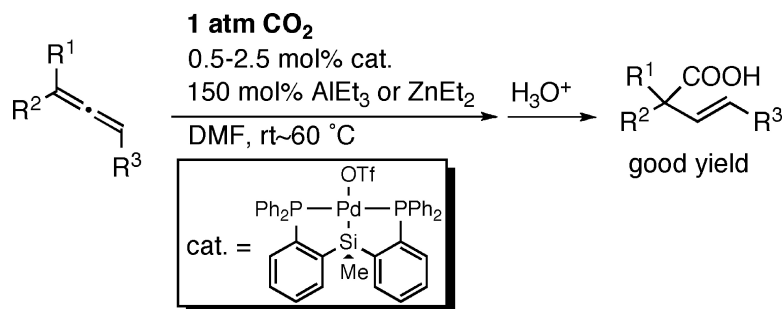


Hydrocarboxylation of Allenes with CO Catalyzed by Silyl Pincer-Type Palladium Complex

Jun Takaya, and Nobuharu Iwasawa

J. Am. Chem. Soc., **2008**, 130 (46), 15254-15255 • DOI: 10.1021/ja806677w • Publication Date (Web): 23 October 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Hydrocarboxylation of Allenes with CO₂ Catalyzed by Silyl Pincer-Type Palladium Complex

Jun Takaya and Nobuharu Iwasawa*

Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8551, Japan

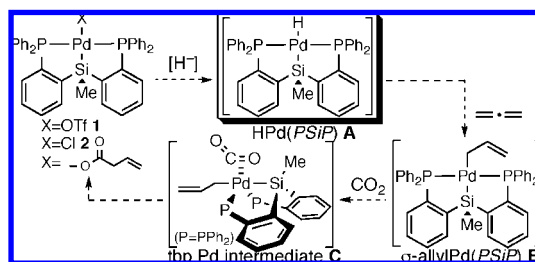
Received August 22, 2008; E-mail: niwasawa@chem.titech.ac.jp

Carboxylation of carbon nucleophiles under atmospheric pressure of CO₂ as an electrophile is highly valuable as a straightforward method for the synthesis of carboxylic acids, and development of its catalytic variant has been a great challenge in synthetic chemistry.¹ Recently several groups including ours reported transition metal catalyzed carboxylation of less nucleophilic organometallic reagents such as allylstannanes,² aryl- or alkenylboronic esters,³ or organozincs;⁴ however, such methodologies usually require preparation of these reagents mostly from the corresponding organic halides. Thus, catalytic generation of nucleophilic organometallic species from easily available unsaturated hydrocarbons would be highly desirable from the standpoint of the atom economical synthetic methodology; however, such catalysis is mostly limited to that based on Ni(0)-promoted oxidative cyclization of rather specific unsaturated hydrocarbons.^{5,6} Herein we report a new approach to the catalytic CO₂-fixation reaction through the generation of σ -allyl palladium species via hydropalladation of allenes, followed by its nucleophilic addition to CO₂ by using a tridentate silyl pincer-type palladium hydride complex **A** as the active catalyst in the presence of an appropriate reducing agent.^{7,8}

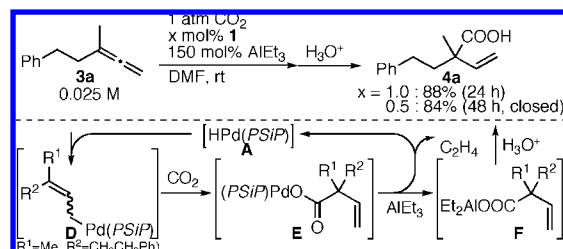
We have designed the reaction based on the following expectations (Scheme 1).⁹ First, the allylpalladium intermediate **B**, generated by hydropalladation of an allene, would take the form of a σ -allyl palladium due to its *PSiP*-tridentate structure and is expected to display nucleophilicity for carboxylation.¹⁰ Second, the nucleophilicity of σ -allylpalladium intermediate **B** would be enhanced due to the strong electron-donating nature and trans influence of the silicon atom at the center of the tridentate pincer backbone.¹¹ Third, a rather strained square planar structure of the *PSiP*-linkage tethered by the benzene ring would facilitate structural change to a trigonal bipyramidal geometry, allowing coordination of CO₂ to realize facile carboxylation as depicted in **C**. Finally, the pincer structure of the complex would retard Pd(0) liberation and avoid side reactions such as oxidative cyclization of allenes promoted by Pd(0).¹²

Examination of appropriate reductants was carried out with 3-methyl-5-phenyl-1,2-pentadiene **3a** under 1 atm of CO₂ in the presence of 1 mol% of *PSiP*-Pd triflate complex **1** in several solvents.^{13,14} After extensive screening of reaction conditions, the use of 150 mol% of AlEt₃ turned out to be the choice of the reducing agent, affording the desired β,γ -unsaturated carboxylic acid **4a** with a quaternary carbon center at the α -position of the carbonyl in 88% yield (Scheme 2).^{15,16} The catalyst loading could be reduced to 0.5 mol% without decreasing the yield (84% after 48 h). Although higher temperature was required, ZnEt₂ also showed good activity as a reductant to give **4a** in 84% yield at 60 °C.¹⁷ γ -Substituted β,γ -unsaturated carboxylic acid, formed by carboxylation at the less substituted carbon of the allyl palladium intermediate, was not observed. The reaction is believed to start with generation of silyl pincer-type palladium hydride complex **A** via transmetalation of AlEt₃ to **1** followed by β -hydride elimination. Hydrometalation of 1,1-disubstituted allene preferentially affords less congested σ -allyl

Scheme 1. Utilization of Silyl Pincer-Type Pd Complex



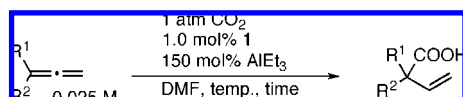
Scheme 2. 1-Catalyzed Hydrocarboxylation of Allene



palladium intermediate **D**, which then undergoes nucleophilic addition to CO₂ at the γ -position of the palladium regioselectively to give carboxylate palladium complex **E**. Finally, a transmetalation/ β -hydride elimination sequence regenerates catalytically active palladium hydride **A** and releases the carboxylation product as its Al-salt **F** (Scheme 2).¹⁸

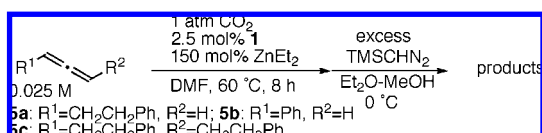
Generality of 1,1-disubstituted allenes was investigated by using 150 mol% of AlEt₃ as the reductant in DMF (Table 1). The reaction of 3-methyl-1,2-butadiene **3b**, Ph-conjugated allene **3c**, and *exo*-vinylidencycloheptane **3g** proceeded smoothly to give corresponding α -quaternary β,γ -unsaturated carboxylic acids in good yield as a single regioisomer (entries 1–2, 6). Another feature of this carboxylation reaction is its high compatibility with various functionalities. Silyl ether **3d**, ester **3e**, ketal **3i**, and carbamate **3h** were successfully converted to the corresponding functionalized carboxylic acids in moderate to excellent yield by using only 1 mol% of catalyst (entries 3, 4, 7, and 8). More importantly, alkene and ketone moieties were not affected under the reaction conditions (entries 5 and 9). High diastereoselectivity was attained when allene **3k** was used (entry 10).¹⁹ Thus, this carboxylation reaction of 1,1-disubstituted allenes provided a highly efficient entry to synthetically useful α -quaternary β,γ -unsaturated carboxylic acids.

Furthermore, this carboxylation was applicable to mono- or 1,3-disubstituted allenes. Although slight modification of reaction conditions was required,²⁰ alkyl- or Ph-substituted allenes **5a**, **5b**, and 1,3-disubstituted allene **5c** reacted smoothly to give α -substituted β,γ -unsaturated carboxylic acids **6a–c** as a major product in reasonable yield in the presence of 1–2.5 mol% of **1** and 150 mol% of ZnEt₂ at 60 °C (Table 2). Interestingly, careful analysis revealed

Table 1. Generality of 1,1-Disubstituted Allenes

entry	allene	conditions	products
1		rt, 48 h	
2 ^a		rt, 24 h	
3		50 °C, 12 h	
4		50 °C, 12 h	
5		rt, 24 h	
6		rt, 24 h	
7		50 °C, 8 h	
8		rt, 48 h	
9		rt, 48 h	
10		rt, 24 h	

^a 2.5 mol% of **1** was employed. ^b dr = 91:9. ^c Isolated as its methyl ester after treatment with TMSCHN₂.

Table 2. Carboxylation of Mono- or Disubstituted Allenes

entry	allene	products
1 ^a		
2 ^b		
3		

^a 1.0 mol% of **1** was employed. ^b Yields were determined as carboxylic acid without esterification. ^c E/Z = 69:31.

that a small amount of γ -substituted β,γ -unsaturated carboxylic acids **7** and α,β -unsaturated acids **8** were obtained, which were regioisomers in the carboxylation and hydrometalation step, respectively.

In conclusion, we have developed a novel catalytic hydrocarboxylation of allenes by utilizing a silyl pincer-type palladium complex as the catalyst. This protocol is highly attractive not only as a CO₂-fixation reaction but also as a methodology for the synthesis of β,γ -unsaturated carboxylic acids due to its wide generality and high efficiency. Detailed mechanistic studies and application of this catalysis to other substrates are ongoing in our group.

Acknowledgment. This research was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. We thank Ms. Sachiyo Kubo for performing X-ray analysis.

Supporting Information Available: Preparative methods and spectral and analytical data of compounds **1–8** and ORTEP diagram

and a CIF file for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Reviews on transition metal-promoted CO₂-fixation reactions; see: (a) Sakakura, T.; Choi, J.-C.; Yasuda, H. *Chem. Rev.* **2007**, *107*, 2365. (b) Yin, X.; Moss, J. R. *Coord. Chem. Rev.* **1999**, *181*, 27. (c) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747.
- (a) Johansson, R.; Wendt, O. F. *Dalton Trans.* **2007**, 488. (b) Shi, M.; Nicholas, K. M. *J. Am. Chem. Soc.* **1997**, *119*, 5057.
- (a) Ukai, K.; Aoki, M.; Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2006**, *128*, 8706. (b) Takaya, J.; Tadami, S.; Ukai, K.; Iwasawa, N. *Org. Lett.* **2008**, *10*, 2697. (c) Ohishi, T.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2008**, *47*, 5792.
- (a) Yeung, C. S.; Dong, V. M. *J. Am. Chem. Soc.* **2008**, *130*, 7826. (b) Ochiai, H.; Jang, M.; Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2008**, *10*, 2681.
- Mori et al. developed nucleophilic carboxylation of allylnickel intermediates generated by Ni(0)-promoted oxidative cyclization of bis(1,3-diene)s or TMS-substituted allenes with CO₂. See: (a) Takimoto, M.; Kawamura, M.; Mori, M.; Sato, Y. *Synlett* **2005**, 2019. (b) Takimoto, M.; Nakamura, Y.; Kimura, K.; Mori, M. *J. Am. Chem. Soc.* **2004**, *126*, 5956. (c) Takimoto, M.; Mori, M. *J. Am. Chem. Soc.* **2002**, *124*, 10008.
- Cu-Catalyzed nucleophilic alkylation of CO₂ using terminal alkynes as substrates was reported; see: (a) Oi, S.; Fukue, Y.; Nemoto, K.; Inoue, Y. *Macromolecules* **1996**, *29*, 2694. (b) Fukue, Y.; Oi, S.; Inoue, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 2091.
- Transition metal catalyzed reactions of allenes with CO₂ were reported although their catalytic activity, scope, yield, and product selectivity were not satisfactory; see: (a) Tsuda, T.; Yamamoto, T.; Saegusa, T. *J. Organomet. Chem.* **1992**, *429*, C46. (b) Dérien, S.; Clinet, J.-C.; Duñach, E.; Périchon, J. *Synlett* **1990**, 361. (c) Sasaki, Y. *J. Mol. Catal.* **1989**, *54*, L9. (d) Aresta, M.; Quaranta, E.; Ciccarese, A. *Cl Mol. Chem.* **1985**, *1*, 283. (e) Döhning, A.; Jolly, P. W. *Tetrahedron Lett.* **1980**, *21*, 3021.
- Reductive allylation of other carbonyl compounds using allene substrates were recently reported; see: (a) Skucas, E.; Bower, J. F.; Krische, M. J. *J. Am. Chem. Soc.* **2007**, *129*, 12678. (b) Bower, J. F.; Skucas, E.; Patman, R. L.; Krische, M. J. *J. Am. Chem. Soc.* **2007**, *129*, 15134. (c) Ngai, M.-Y.; Skucas, E.; Krische, M. J. *Org. Lett.* **2008**, *10*, 2705.
- Synthesis of several tridentate *PSiP*-pincer complexes have been reported although they have rarely been used as a catalyst in synthetic organic chemistry; see: (a) Gossage, R. A.; McLennan, G. D.; Stobart, S. R. *Inorg. Chem.* **1996**, *35*, 1729. (b) Brost, R. D.; Bruce, G. C.; Joslin, F. L.; Stobart, S. R. *Organometallics* **1997**, *16*, 5669. (c) MacInnis, M. C.; MacLean, D. F.; Lundgren, R. J.; McDonald, R.; Turculet, L. *Organometallics* **2007**, *26*, 6522. and references cited therein. See also: (d) Balakrishna, M. S.; Chandrasekaran, P.; George, P. P. *Coord. Chem. Rev.* **2003**, *241*, 87. (e) Minato, M.; Zhou, D.-Y.; Sumiura, K.-i.; Hirabayashi, R.; Yamaguchi, Y.; Ito, T. *Chem. Commun.* **2001**, 2654. (f) Minato, M.; Matsumoto, T.; Ichikawa, M.; Ito, T. *Chem. Commun.* **2003**, 2968. (g) Korshin, E. E.; Leitus, G.; Shimon, L. J. W.; Konstantinovski, L.; Milstein, D. *Inorg. Chem.* **2008**, *47*, 7177.
- Allyl palladium complexes bearing *PCP*-pincer ligand are reported to act as nucleophilic allylation catalyst; see: Szabó, K. J. *Synlett* **2006**, 811.
- See ref 9 and references cited therein.
- Oligomerization of allene was often observed as a side reaction; see ref 7e.
- 1** was synthesized in good yield by ligand exchange of CIPd(*PSiP*) **2** with AgOTf. The structure of **1** was confirmed by X-ray analysis. For detailed procedure and ORTEP diagram, see Supporting Information.
- Turculet and co-workers reported preparation of **2** during this research was in progress; see ref 9c.
- Other solvents such as toluene, 1,4-dioxane, and THF resulted in lower conversion under the same conditions.
- 2** did not show catalytic activity under the same conditions probably due to its lower activity for initial transmetalation with AlEt₃.
- Other reducing agents such as Et₃SiH and BEt₃ did not afford the product.
- The possibility that the carboxylation occurs not with **D** but with an allylaluminum intermediate generated by metal exchange should be considered. However, the reaction in Scheme 2 just without CO₂ afforded only 9% of 3-methyl-5-phenyl-1-pentene, and 78% of **3a** was recovered. Even when the same reaction was run in the presence of diethylaluminum carboxylate, nearly the same result was obtained. These results strongly suggest that the exchange of allylpalladium to allylaluminum did not occur to an appreciable amount under the present reaction conditions and carboxylation occurs mainly with the allylpalladium intermediate.
- The stereochemistry was not determined.
- The use of AlEt₃ caused isomerization of the product to α,β -unsaturated carboxylic acid.

JA806677W